

GAS PHASE GLYCEROL DEHYDRATION TO ACROLEIN OVER
SUPPORTED SILICOTUNGSTIC ACID CATALYST

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A thesis submitted in fulfilment of the
requirements for the award of the degree of
Doctor of Philosophy (Chemical Engineering)

Faculty of Chemical Engineering
Universiti Teknologi Malaysia

OCTOBER 2015

TO MY BELOVED WIFE AND MOTHER

ACKNOWLEDGEMENT

First of all, I would like to thank Allah for giving me the strength, perseverance and intention to go through and complete my study.

I would like to express my sincere gratitude to my respected supervisor Prof. Dr. Nor Aishah Saidina Amin for her help, support, and guidance. I owe her a lot for what she taught me during these years. Without her valuable guidance this study could never have reached its completion.

Last but not least, I wish to express my deepest gratitude and love for my beloved family members especially my wife, mother, father and mother-in-law, and brother for their utmost support, patience and understanding throughout my PhD study.

ABSTRACT

Due to the various environmental concerns, a steep hike in fossil fuel price and an increasing demand of non-renewable fossil fuels consumption, the bio-based gas-phase dehydration of glycerol to acrolein has attracted much attention recently. Thus, the gas phase dehydration of glycerol to acrolein over two groups of supported silicotungstic acid on aluminum oxide (Al_2O_3) nanoparticle and zirconium dioxide catalyst is being investigated in this study. The catalysts were characterized by, X-ray diffraction, Fourier transform infrared spectroscopy, field-emission scanning electron microscopy and energy dispersive X-ray techniques, temperature programmed desorption, thermogravimetric analysis, and elemental analyzer. The characterization results revealed that Al_2O_3 nanoparticle loading increased thermal stability, pore diameter, and specific surface area of the synthesized catalysts. Optimization by response surface methodology revealed the highest acrolein selectivity of 88.5% at 97% glycerol conversion was obtained over 30HZ-20A catalyst with turnover frequency being 136 h^{-1} in 3 h for glycerol feed concentration of 10.3 wt% and 0.5 g catalyst at $300 \text{ }^\circ\text{C}$. Coke deposition has no significant effect on the catalyst activity due to the large catalyst pore diameter ($> 27 \text{ nm}$). The prepared catalysts were highly active and selective for acrolein production even after 40 h without any needs for gas co-feeding or application of noble metals. In addition, the kinetic study results demonstrated that glycerol dehydration to acrolein followed first-order rate with the activation energy (E_a) of 27.5 kJ/mol and frequency factor (A) of $5.35 \times 10^5 \text{ s}^{-1}$. Finally, the theoretical and experimental approaches confirmed no internal mass transfer limitation in glycerol dehydration reaction with catalyst pellet sizes of $d_p = 2\text{-}4$ and $5\text{-}7 \text{ }\mu\text{m}$ due to effectiveness factor equal to 1 ($\eta = 1$). Calculation of the overall effectiveness factor (η_o) also confirmed the absence of external diffusion in presence of catalysts with pellet size of $d_p < 7 \text{ }\mu\text{m}$.

ABSTRAK

Disebabkan oleh pelbagai kebimbangan terhadap alam sekitar, peningkatan mendadak harga bahan api fosil dan peningkatan permintaan penggunaan bahan api fosil tidak boleh diperbaharui, penyahhidratan fasa gas gliserol kepada akrolein berdasarkan bahan bio telah menarik perhatian ramai baru-baru ini. Oleh itu, penyahhidratan fasa gas gliserol kepada akrolein menggunakan dua kumpulan asid silikotungstik yang disokong oleh partikel nano aluminium oksida (Al_2O_3) dan pemangkin zirkonium dioksida telah dikaji dalam kajian ini. Pemangkin-pemangkin dicirikan dengan menggunakan teknik pembelauan sinar-X, spektroskopi inframerah transformasi Fourier, mikroskop elektron imbasan pemancaran medan dan sebaran tenaga sinar-X, penyaherapan suhu berprogram, analisis termogravimetrik, dan penganalisis unsur. Keputusan pencirian menunjukkan bahawa muatan partikel nano Al_2O_3 menunjukkan kestabilan terma, diameter liang, dan luas permukaan spesifik bagi pemangkin yang disintesis. Pengoptimuman oleh kaedah tindak balas permukaan menunjukkan kepilihan akrolein tertinggi iaitu 88.5% pada penukaran gliserol 97% telah diperolehi menggunakan pemangkin 30HZ-20A dengan frekuensi pusingan balik 136 h^{-1} dalam tempoh 3 jam bagi kepekatan suapan gliserol 10.3 wt% dan pemangkin 0.5 g pada $300 \text{ }^\circ\text{C}$. Pengekutan kok tidak mempunyai kesan signifikan terhadap aktiviti pemangkin disebabkan oleh diameter liang pemangkin yang besar ($> 27 \text{ nm}$). Pemangkin yang disediakan adalah sangat aktif dan selektif bagi penghasilan akrolein walaupun setelah 40 jam tanpa sebarang keperluan untuk penyusunan bersama gas atau aplikasi logam adi. Di samping itu, keputusan kajian kinetik menunjukkan penyahhidratan gliserol kepada akrolein mengikut kadar tertib pertama dengan tenaga pengaktifan (E_a) 27.5 kJ/mol dan faktor kekerapan (A) $5.35 \times 10^5 \text{ s}^{-1}$. Akhir sekali, pendekatan teori dan eksperimen mengesahkan tiada pengehadan pemindahan jisim dalaman bagi tindak balas penyahhidratan gliserol dengan saiz pelet pemangkin $d_p = 2-4$ dan $5-7 \text{ }\mu\text{m}$ disebabkan oleh faktor keberkesanan adalah bersamaan dengan 1 ($=1$). Pengiraan faktor keberkesanan keseluruhan (η) juga mengesahkan ketiadaan peresapan luaran dalam kehadiran pemangkin dengan saiz pelet $d_p < 7 \text{ }\mu\text{m}$.

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LIST OF ABBREVIATIONS

ANOVA	-	Analysis of Variance
BET	-	Brunauer-Emmett-Teller
FID	-	Flame ionization detector
GC	-	Gas chromatography
GHSV	-	Gas-hourly-space-velocity
HPA	-	Heteropoly acid
HSiW	-	Silicotungstic acid
PBR	-	Packed bed reactor
Py-Ir	-	Pyridine infrared spectroscopy
TCD	-	Thermal conductivity detector
TOS	-	Time-on-stream
TPD	-	Temperature programmed oxidation
TEM	-	Transmission Electron Microscope
TGA	-	Thermogravimetric analysis
XRD	-	X-ray diffraction
xHZ	-	x wt% of HSiW loading on ZrO ₂
yHA	-	y wt% of HSiW loading on Al ₂ O ₃

LIST OF SYMBOLS

E_a	-	Activation Energy
X	-	Conversion
D, d	-	Diameter
ρ	-	Density
θ	-	Diffraction Angle
u	-	Expansion factor
Y	-	Effectiveness Factor
D_{eff}	-	Effective Diffusivity
A	-	Frequency Factor
l	-	Length
m	-	Mass
k_C	-	Mass Transfer Coefficient
$ $	-	Molar Ratio of Solvent to Glycerol
	-	Overall Effectiveness Factor
P	-	Pressure
v	-	Pellet Porosity
r	-	Radius
Re	-	Reynolds Number
k	-	Reaction Rate Constant
S_C	-	Schmidt Number
Sh	-	Sherwood Number
T	-	Temperature
w_1	-	Thiele Modulus
\ddagger	-	Tortuosity
V	-	Volume
λ	-	X-Ray Wavelength

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CHAPTER 1

INTRODUCTION

1.1 Background of Research

Relentless environmental concerns, steep hike in fossil fuel price, and increasing demand of non-renewable fossil fuel consumption have led to dramatic surge in the global search for alternative energy, particularly biodiesel (Sannita *et al.*, 2012; Meher *et al.*, 2013). Indeed, biodiesel significantly decreases engine emissions such as sulfur oxides (100%), un-burned hydrocarbons (68%), and polycyclic aromatic hydrocarbons (80-90%). Many parts of the world have devised plans to enhance their biodiesel production. Europe and USA, for instance, produced 7.8 and 2.3 million ton biodiesel in 2008, respectively and they planned to double their production by 2012 (Katryniok *et al.*, 2010a). In addition, it is estimated that the global biodiesel market will increase significantly to 37 billion gallon by 2016 (Saxena *et al.*, 2009).

The huge amount of biodiesel production worldwide directly affects glycerol availability, since 10% of the total transesterification process production is glycerol (Izquierdo *et al.*, 2012). The surplus offers great opportunities for researchers to use glycerol as a bio-renewable source for value-added chemical production. According to recent studies, glycerol was acknowledged as one of the top 12 most important bio-based chemicals in the world (Werpy and Petersen, 2004) and it will become the major chemical for future bio-refineries. Indeed, the application of glycerol for the

production of more than 2000 products was reported recently (Garcia *et al.*, 2014). Many researchers have demonstrated that glycerol, as the byproduct can decrease biodiesel (B100) production costs by half from 0.63 to 0.35 US \$ per liter (Tyson *et al.*, 2004; Claude, 1999). Nevertheless, glycerol can be produced through different processes such as (1) fatty acid production, (2) microbial fermentation, (3) soap manufacture, (4) biodiesel production and (5) propylene oxide synthesis. In addition, glycerol can be produced by the fermentation of sugars (glucose and fructose) and industrial conversion of lignocelluloses into ethanol (Gong *et al.*, 2000; Rogers *et al.*, 2005).

Glycerol purity is the key factor for its industrial application. Traditionally, industrial biodiesel plants using mineral acids (H_2SO_4 , HCl) and alkali (NaOH , KOH) catalysts. Thus, the glycerol produced by conventional processes include other products such as methanol, water, residual catalyst, free fatty acids, un-reacted mono-, di-, and tri-glycerides, methyl ester and various organic and inorganic compounds (Matter Organic Non-Glycerol (MONG)) (Yori *et al.*, 2007; Chiu *et al.*, 2005). As a result, low quality glycerol requires some treatment, including the neutralization by phosphoric acid (H_3PO_4) or recycling in order to eliminate the excess methanol, catalyst and soap. The final glycerol with approximately 80 - 95% purity will be sold to the industrial refineries at low cost (Tyson *et al.*, 2004; Werpy and Petersen, 2004). However, the purification processes are costly and uneconomical. Hence, some industries prefer to burn the low quality glycerol as waste material and use pure (>98.5%) glycerol instead of purified crude glycerol. As a result, more than 150,000 - 250,000 metric tons of crude glycerol was tragically burnt in 2006, wasting one of the most valuable organic raw materials (McCoy, 2006).

The current trend sees majority of researchers focused on the heterogeneous catalyst application for biodiesel production for higher quality biodiesel and glycerol production. Bournay *et al.*, (2005) investigated biodiesel production in a continuous process by the zinc and aluminum (Zn-Al) mixed oxides as heterogeneous solid catalyst. They reported 98.3% and 98% purity for the final biodiesel and glycerol,

respectively. As a result, their catalytic process could eliminate all the costly treatment and purification processes for the direct application of the produced glycerol in pharmaceutical, cosmetics and food industries (Bournay *et al.*, 2005). The industrial glycerol utilization for value-added chemicals attracted much attention, not only due to the surplus of glycerol available, but also because glycerol is bio-sustainable, non-toxic, and biodegradable. The multi-functional structure and physico-chemical characteristics of glycerol lead to various applications of glycerol in different reaction pathways (Chiu *et al.*, 2005; Bournay *et al.*, 2005; Wang *et al.*, 2001; Chowdury and Fouky, 1993).

The applications of glycerol in our daily life are illustrated in Figure 1.1. Glycerol is being used for moisturizer, sweetener or food and drinks preservative. Since glycerol has a non-toxic nature it is also widely used in cosmetics and toiletries. Moreover, glycerol is also utilized in paper and printing industry for softening and reducing shrinkage during paper manufacturing. In the tobacco industry, glycerol is being used to prevent breaking and crumbling during cigarette processing while it also adds flavor to tobacco.

There are two possible categories for industrial (large scale) application of glycerol. The first is the utilization of glycerol for obtaining commodities such as hydrochlorination of glycerol for chlorohydrins, an important intermediate for epichloridrin production and dehydration of glycerol to acrolein followed by oxidation step for acrylic acid production.

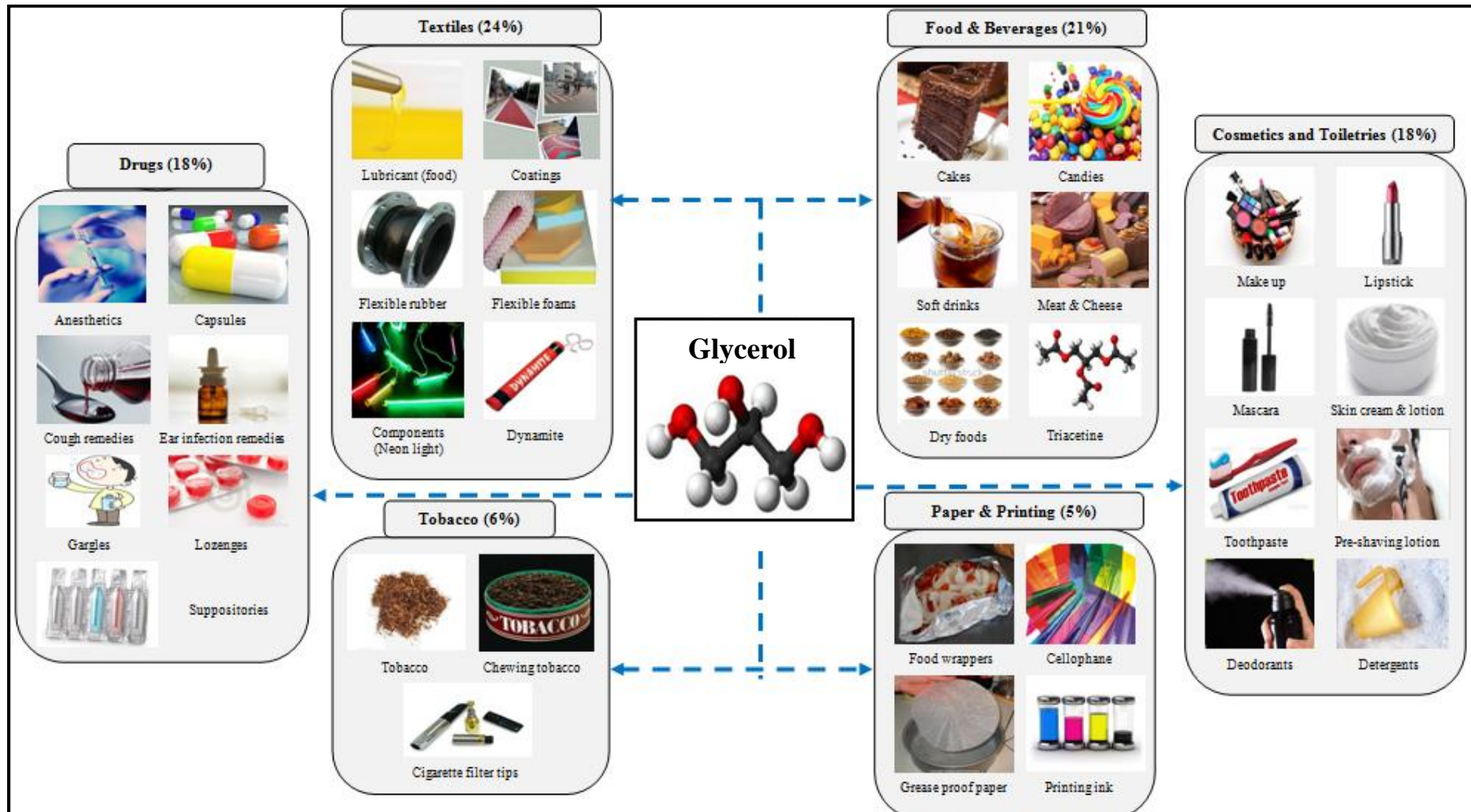


Figure 1.1 Glycerol distributions by application

The other category is the production of oxygenated additives for fuels from glycerol such as: esters (triacetin) (Melero *et al.*, 2007), ethers (glycerol isobutyl ethers) (Behr and Obendorf, 2003; Jaecker-Voirol *et al.*, 2008; Di Serio *et al.*, 2010), ketals (Crotti *et al.*, 2010), and acetals (Crotti *et al.*, 2010; Silva *et al.*, 2010). The etherification of glycerol for production of a mixture of di- and tri-butyl ethers of glycerin (h-GTBE) is the most promising reaction since it is a new additive for gasoline and h-GTBE improves the octane and decreases the pour point, cloud point and diesel viscosity. Figure 1.2 summarizes several materials that can be produced from glycerol by various processes.

The conventional method for acrolein production is a selective oxidation of propylene in the presence of complex BiMoO_x based catalyst with approximately 85% acrolein selectivity at 95% propylene conversion (Keulks, *et al.*, 1979). However, petrochemical exhaustion is foreseen in the near future. Therefore, the production of the most important industrial materials such as acrolein from sustainable and renewable resource is prevalent recently. The main obstacle for such an industrial application is the economical matters. According to the recent reports, the production of acrolein from glycerol can be commercialized if the glycerol price becomes less than 300 US \$/t (Corma *et al.*, 2008). The controlling factor is the application of the low cost crude glycerol that was only 100 US \$/t in 2010 in contrast with refined glycerol which was 500-550 US \$/t in the same year.

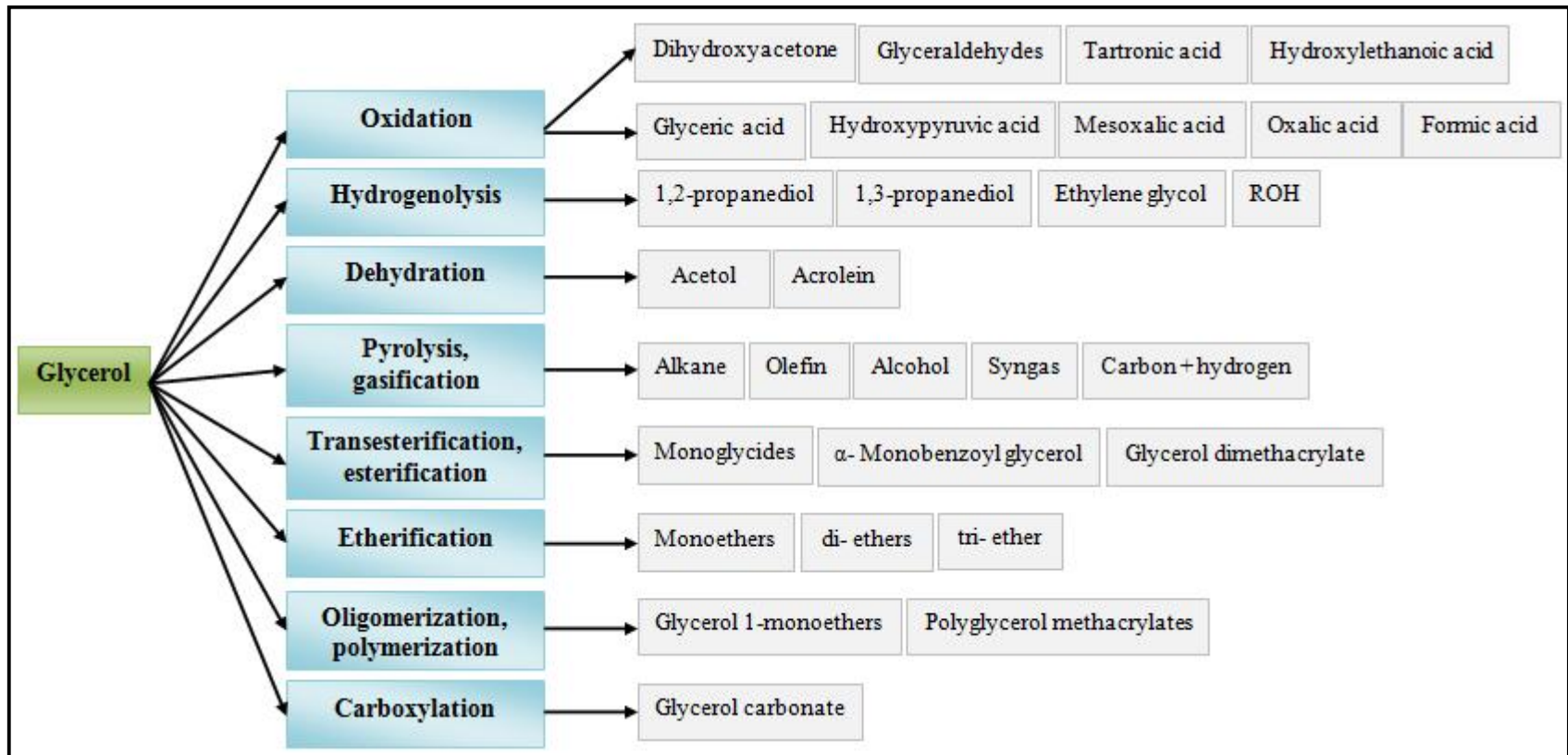


Figure 1.2 Glycerol conversion methods for different value-added chemicals production

Acrolein is highly toxic; therefore, it should be directly converted into other value added chemicals such as acrylic acid, which is used to produce sodium polyacrylate. The polyacrylate is a superabsorbent polymer (SAP) used in hygienic products such as diapers. This material can extremely absorb liquids (more than 500 times of its weight) (Horie *et al.*, 2004). In 2010, it was estimated that SAP has an annual market of 1.9 million tones. The other acrolein application is in methionine production from 3-methylthio-propionaldehyde as an intermediate. The methionine improves animal growth rate and so it is widely used in meat production. In addition, methionine is a very important amino-acid that cannot be produced by living organisms. Due to its low production rate (only 500 kt/yr), large scale synthesis is desirable since the worldwide meat consumption will increase by 3 to 7% in the near future (Malveda *et al.*, 2006). Figure 1.3 shows the all possible chemicals that can be produce from acrolein.

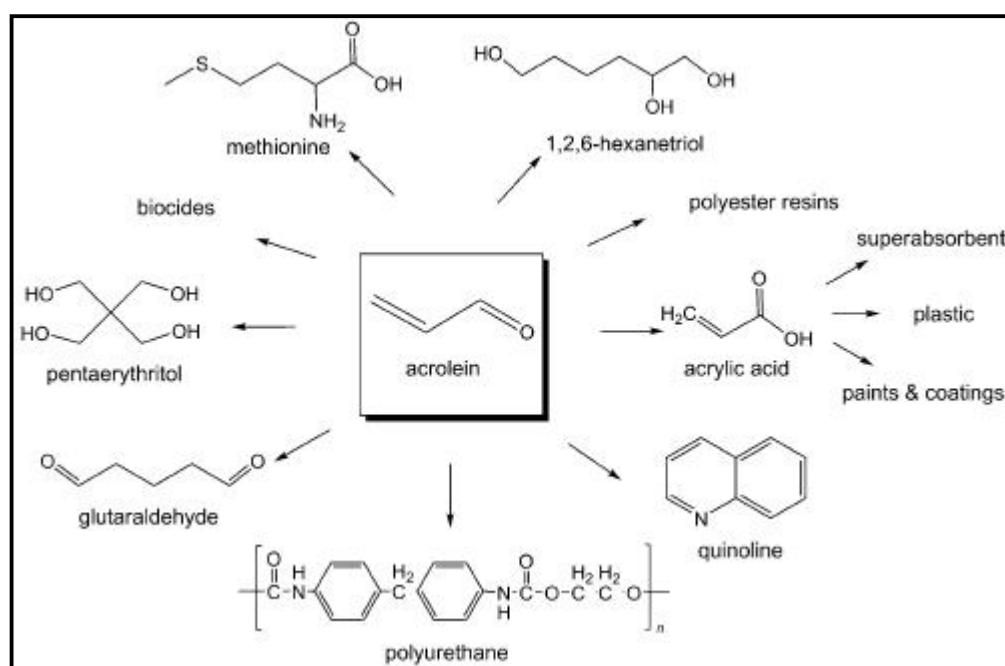


Figure 1.3 Possible chemicals that can be produce from acrolein (Liu *et al.*, 2012)

1.2 Problem Statement

The partial oxidation of propylene by multi component metal catalysts is the conventional methods for acrolein production. However, this method suffered from difficult control of selectivity and yield of products and propylene oxidation is a primary manufacturing method (Liu *et al.*, 2012). In addition, propylene is non-renewable and expensive due to its highly dependent to the fossil fuel price. Thus, glycerol can be used as a bio-based source instead of petroleum-based process to decrease various environmental concerns and even production costs of acrolein.

The catalytic dehydration of glycerol to acrolein in the gas phase uses various catalysts such as supported heteropoly acids, zeolites, and mixed metal oxides, but still there is no catalyst with the long-term stability without severe deactivation and with the promise of industrialization (Haider *et al.*, 2012). Moreover, the conventional liquid phase glycerol dehydration to acrolein mostly used homogeneous catalysts (H_2SO_4) at supercritical conditions. The application of some heterogeneous catalysts was reported recently, however, the mixture of powerful super acids and supercritical conditions is highly corrosive and can seriously damage the reactor vessels (Ott *et al.*, 2006). Therefore, the application of the supported heteropoly acid catalysts at ambient pressure in a continuous system is studied in this research to increase the activity as well as long life stability of catalyst.

Catalyst deactivation as a result of coke formation is the most common drawback for all the tested catalyst in fixed bed reactors during glycerol dehydration to acrolein. Gas Co-feeding and application of noble metals are reported as conventional approaches for slowing down the deactivation rate of catalyst (Haider *et al.*, 2012). However, recent studies demonstrated that catalyst characteristics (acidity and pore size) are the main factors which can seriously decrease the effect of coke formation on catalyst surface (Yun *et al.*, 2014). Thus, the improvements of physicochemical characteristics of prepared catalysts are evaluated to increase the long life stability and activity of catalyst in this research.

The kinetic parameters of glycerol dehydration to acrolein are still unknown in the majority of cases and all the previous studies performed in the supercritical conditions (Watanabe *et al.*, 2007; Ott *et al.*, 2006; Qadariyah *et al.*, 2011). The applications of gas-phase dehydration of glycerol to acrolein in the presence of heterogeneous catalysts (HPAs, zeolites, and mixed metal oxides) have been reported by a lot of researchers recently (Yadav *et al.*, 2013; Danov *et al.*, 2015; Dalil *et al.*, 2015). Therefore, finding the kinetic parameters (reaction rate constant (k), activation energy (E_a) and frequency factor (A)) at ambient pressure in a continuous system is the key component for simulation and particularly economical industrialization of a bio-based acrolein production process.

Fully utilization of catalyst surface in a heterogeneous catalytic reaction depends on the mass transfer limitations inside the pore structure in the pellets (Baek *et al.*, 2014). Based on our knowledge, there has been no study on internal and external mass transfer limitations in gas-phase glycerol dehydration to acrolein in a continuous system using heterogeneous catalysts. Therefore, dimensionless parameters known as the Thiele modules (w_i), effectiveness factor (η), and overall effectiveness factor (η_o) determined to investigate the efficiency of catalyst utilization.

1.3 Research Hypothesis

- 1) Glycerol can be converted into acrolein during a dehydration process. Silicotungstic acid (HSiW) has been identified as the potential catalyst for this process due to its strong acidic sites (Bronsted) and high water tolerance abilities (Katryniok *et al.*, 2012). Modification of HSiW with selected metal oxide (ZrO_2) may increase the activity of the catalyst, thus hypothetically, active acid sites that create an acidic environment in the supported HSiW catalyst can increase glycerol conversion and acrolein selectivity by tuning the strong acidic sites to the medium acidic sites.

- 2) Supported HSiW on ZrO₂ catalyst should have low surface area because HSiW classified as non-porous materials and ZrO₂ also have a very small surface area. Thus, Al₂O₃ nanoparticlea are added as the third component to the catalyst in order to increase the surface area and pore diameter of the final catalyst. Consequently, the long life stability of catalyst should be increased due to the presence of large pore diameter and pore volume. Yun *et al.* (2014) reported that large pore diameter is the main factor which can significantly decrease the effect of the coke deposition and catalyst deactivation process. Thus, the final catalyst does not need any types of regeneration methods such as hydrogen or oxygen cofeeding or noble metal application to enhance its long-term stability.

1.4 Research Objectives

- 1) To synthesize and characterize new supported silicotungstic acid catalysts using aluminum oxide nanoparticles and zirconium dioxide.
- 2) To optimize the reaction parameter values by response surface methodology (RSM).
- 3) To determine the kinetic parameters in gas phase dehydration of glycerol to acrolein.
- 4) To determine the internal and external diffusions inside the pore structures by theoretical and experimental approaches.

1.5 Research Scopes

The gas phase dehydration of glycerol to acrolein was investigated in a continuous tubular reactor using supported silicotungstic acid (HSiW) by zirconium

oxide (ZrO_2) and aluminum oxide (Al_2O_3) nanoparticles which were synthesized by incipient-wetness impregnation method.

The prepared catalysts are characterized by nitrogen adsorption-desorption (BET), X-ray diffraction (XRD), fourier transform infrared spectroscopy (FTIR), Pyridine adsorption (Py-Ir), field-emission scanning electron microscopy and energy dispersive X-Ray techniques (FESEM-EDX), temperature programmed desorption (NH_3 -TPD), thermogravimetric analysis (TGA), Transmission Electron Microscope (TEM), and elemental analyzer (EA) to evaluate their physicochemical characteristics.

The prepared samples were evaluated under different reaction temperatures (270 - 330 °C), catalyst loading (0.1 – 0.9 g), glycerol concentration (0.5 – 20 wt%), 2 ml/h flow rate of glycerol in the feed, and 1200 ml/h flow rate of carrier gas (N_2). Furthermore, the investigation of the reaction route, side products and the relationships between the properties of the catalysts and their performance in acrolein production represent the scope of this work. In addition, the response surface methodology (RSM) is used for the optimization and modeling of processes.

The initial reaction rate constant (k) is determined at four different reaction temperatures (280, 300, 320, and 340 °C) and for each reaction temperature a series of experiments were performed with various feed flow rates (2, 5, and 10 ml/h). The kinetic parameters such as activation energy (E_a), and frequency factor (A) are needed for process simulation and scale-up purposes for further investment on large scale (industrial) application and commercialization.

The existence of the internal and external diffusions was investigated at various catalyst pellet size (2 - 45 μm), catalytic bed volume (2 - 10 ml), and gas mass flow rate (2.55 - 25.2 g/h) by the theoretical and experimental approaches.

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APPENDIX A

LIST OF PUBLICATIONS

A.1. Journal Papers

1. **Talebian-Kiakalaieh, A;** Amin, N.A.S; Hezaveh, H. Glycerol for renewable acrolein production by catalytic dehydration, *Renewable and Sustainable Energy Reviews*, 2014; 40; 28-59. (IF=5.9).
2. **Talebian-Kiakalaieh, A;** Amin, N.A.S. Supported silicotungstic acid on zirconia catalyst for gas phase dehydration of glycerol to acrolein, *Catalysis Today*, 2015; 256: 315-324. (IF=3.9).
3. **Talebian-Kiakalaieh, A;** Amin, N.A.S. Theoretical and Experimental Evaluation of Mass Transfer Limitation in Gas Phase Dehydration of Glycerol to Acrolein over Supported HSiW Catalyst, *Journal of the Taiwan Institute of Chemical Engineers* (2015), <http://dx.doi.org/10.1016/j.jtice.2015.07.011>. (IF= 3.0)
4. **Talebian-Kiakalaieh, A;** Amin, N.A.S. Kinetic modeling, thermodynamic and mass transfer studies of gas-phase glycerol dehydration to acrolein over supported silicotungstic acid catalyst, *Industrial and Engineering Chemistry Research*, 2015; 54: 8113-8121. (IF = 2.6)

A.2. Conference

1. **Talebian-Kiakalaieh, A;** Amin, N.A.S. Supported silicotungstic acid on zirconia catalyst for gas phase dehydration of glycerol to acrolein. *21st International Congress of Chemical and Process Engineering CHISA 2014, 23-27 August 2014 Prague, Czech Republic.*